Mujtaba, Muhammad; Fernandes Fraceto, Leonardo; Fazeli, Mahyar; Mukherjee, Sritama; Savassa, Susilaine Maira; Araujo de Medeiros, Gerson; do Espírito Santo Pereira, Anderson; Mancini, Sandro Donnini; Lipponen, Juha; Vilaplana, Francisco

Lignocellulosic biomass from agricultural waste to the circular economy: a review with focus on biofuels, biocomposites and bioplastics

Published in:
Journal of Cleaner Production

DOI:
10.1016/j.jclepro.2023.136815

Published: 20/05/2023

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Review

Lignocellulosic biomass from agricultural waste to the circular economy: a review with focus on biofuels, biocomposites and bioplastics

Muhammad Mujtaba a,b,1,*, Leonardo Fernandes Fraceto c, **, Mahyar Fazeli b, Sritama Mukherjee b,e, Susilaine Maira Savassa c, Gerson Araujo de Medeiros c, Anderson do Espírito Santo Pereira c, Sandro Donnini Mancini c, Juha Lipponen b, Francisco Vilaplana d,f,***

a VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, Espoo, FI-02044, Finland
b Aalto University, Bioproducts, and Biosystems, 02150, Espoo, Finland
c Department of Environmental Engineering, Institute of Science and Technology of Sorocaba, São Paulo State University (UNESP), Avenida Três de Maço, 511, CEP 18087-180, Sorocaba, São Paulo, Brazil
d Division of Glycoscience, Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology, and Health, KTH Royal Institute of Technology, Stockholm, Sweden
e Division of Fiber and Polymer Technology, CBH, KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden
f Department of Environmental Engineering, Institute of Science and Technology of Sorocaba, São Paulo State University (UNESP), Avenida Três de Maço, 511, CEP 18087-180, Sorocaba, São Paulo, Brazil

** Corresponding author. S. Maira Savassa, savassa@unesp.br (S. Maira Savassa), franvila@kth.se (F. Vilaplana).
*** Corresponding author. Division of Glycoscience, Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology, and Health, KTH Royal Institute of Technology, Stockholm, Sweden.

Handling Editor: Maria Teresa Moreira

ARTICLE INFO

Keywords:
Sustainability
Biofuels
Bioplastics
Biorefineries

ABSTRACT

Industries are working to minimize their reliance on petrochemicals and petroleum-based industrial components and replace them with biobased, sustainable, and environmentally friendly alternatives due to the global warming emergency caused by the uncontrolled production of greenhouse gases. The agricultural waste provides large volumes of lignocellulosic biomass, a sustainable resource material to develop a wide portfolio of bioproducts. Recent developments in integrated biorefineries have enhanced the utilization of waste lignocellulose components to generate biofuels, platform chemicals, resins, bioplastics, additives, and other biobased materials for a variety of applications. Here in this review, we have summarized recent advancements in the processing of lignocellulosic biomass from agricultural waste. Additionally, this review thoroughly discussed the recent technological advancements in the utilization of various lignocellulose biomass constituents for biofuels, biocomposites, and bioplastics. Finally, an assessment of the currently existing literature gaps and prospective future perspectives for the development of lignocellulosic biomass from agricultural waste has been conducted.

1. Introduction

The concepts of circular economy and bioeconomy have been introduced as alternative economic production models to encourage sustainable growth and development (Ferreira Gregorio et al., 2018). The main idea behind these models is to accomplish the synergy between growing economies, societies, and the environment (Stephenson and Damerell, 2022). By applying these key concepts of circular...
economy and bioeconomy, policies can be drawn up for the successful implementation of 17 sustainable developmental goals that were adopted by member states of the United nations in 2015 (Walker, 2021). The unsustainable consumption of global resources is not only posing a huge threat to the environment but also creating a negative impact on the quality of human lives. This global masterplan draws attention to the transformation of economic, political, and financial to improve the overall quality of human life worldwide (Mehmood, 2021). With an ever-increasing material footprint globally, the world’s major industrial producers are striving to adopt such production policies that help them to reduce their dependence on nonrenewable resources. Applying common principles of circular economy and bioeconomy helps to reduce the impact on natural resources and uplifting of society by enhancing the quality of life and creating new jobs. The European Union has a special focus on the development and adoption of policies that promote the use of renewable resources for energy and product development (‘D’Adamo et al., 2022). Similarly, China is focusing on the implementation of policies based on circular economy practices (Yu et al., 2021).

Lignocellulose-based bioeconomy is gaining attention from both researchers and industries as it can offer renewable feedstock for many application areas such as energy, food, nutrition, the chemical industry, etc., (Banu et al., 2021). Lignocellulose biomass (LCB) arises from agricultural and forest residues, organic solid waste from recycling stations, paper, wood, and pulp. According to recent statistics, globally the annual production of lignocellulose biomass is approximately 181.5 billion tons, out of which only 8.2 billion tons of lignocellulose biomass is utilized by different application areas (Singh et al., 2022). This demonstrates the untapped availability of plant-based biomass for transformation into a wide portfolio of bioproducts for basically all application sectors. Indeed, advancements in lignocellulose biorefinery are paving the path for producing sustainable energy, bioplastics, and other bioproducts from renewable and environmentally friendly lignocellulose biomass. LCB can be easily converted into bioenergy through thermochemical (pyrolysis, combustion, gasification, and liquefaction) and biochemical (treatment with microorganisms and enzymes) conversion routes (Patel and Shah, 2021). As per some reports, compared to other renewable resources, lignocellulose biomass serves as the primary resource for producing biofuels for air, road, and water transport. Besides, lignocellulose biomass has the potential to substitute petroleum-based plastics and other petrochemical materials fully or partially. Lignocellulose-based bio-composites have been successfully employed for different purposes, such as inks for additive manufacturing, multifunctional substrates in environmental remediation, medical applications, cleaner production, etc., (Usmani et al., 2021).

So far, several review articles have discussed lignocellulosic biomass from agricultural waste in terms of pretreatment, processing, chemical components, conversion, etc. However, reports giving a holistic picture of lignocellulose biomass from pretreatment to applications and its impact on the circular economy are scarce. This review provides a deeper understanding of the importance of lignocellulose biomass from agricultural waste to a modern circular economy. The review provides an outline of realistic biorefinery biomaterials derived from agro-waste and summarizes the final progress in biobased processes for lignocellulosic waste utilization (biofuels, bioplastics, and biocomposites for environmental and medical applications).

2. Importance of agricultural waste in a circular economy

With the growth of the world population and the growing demand for agricultural production, there is also an increase in agricultural waste. This agricultural waste production is becoming a problem that must be worked on. In China, a giant in the agro scenario, the annual agro-waste reaches around 0.9 billion t. The simple discard of this agro-waste can negatively impact the environment by contaminating the soil and water sources (Yu et al., 2023). Different alternatives are being considered for the use of these agricultural residues for energy production.

In the modern world, the immense need for energy has been fulfilled by non-renewable fossil fuels. As an alternative to this, novel renewable sources of fuels are among the burning quests of modern-day research. Among the renewable resources for energy, biomass has been projected as a potential candidate for the substitution of crude oil-based refineries. As is known, carbon biomass is a carbon-neutral, widely available, and most importantly renewable feedstock to produce different chemicals and fuels.

The Circular economy is an alternative industry model, aiming for sustainable development. This new business model is a designer based on economy and environment promoting development, profit, and environmental protection (Andoiz et al., 2023). For example, industrial residues are not discarded, on the contrary, these residues can be transformed into raw materials for other products (Nattassha et al., 2020).

A circular economy can be defined under two governing principles; it increases the value of raw material by enhancing its conversion to product, and with responsible product design, the loss of service time is reduced. The closed loop idea (circular) aims the inessential flow of technical and biological resources, like agricultural waste, in the value loop though keeping products, components, and resources at their maximum value always and plummeting waste to the least possible level (EMF, 2013). As it is known that circular economy is an emerging concept which, still in the academy and literature, there is a lack of consensus on its theoretical definition. This can be attributed to the fact that the circular economy is the result of changes in policy frameworks and legislation, not academic research. Recycling and reprocessing the ingredients of a product offers the opportunity to extend the utility of material even further. In other words, the hidden potential of a material is further exploited rather than just wasting it. Therefore, industries are looking for materials that offer infinite properties such as recyclability and reusability, and all this can be possible by adopting the principles of the circular economy.

According to a recent IEA 2017 report, the total share of biomass in the energy supply is 9%. Various types of biomasses have been generated through agricultural activities such as animal manure and slurries, post-harvest plant residues, non-marketable products, products of no market value, wastes from low or untreated animals, waste from olives and grape processing lines, and milk-based waste, etc. The lack of a proper reuse policy leads to uncontrolled extraction of these bioresources for production and consumption and hails the regeneration of the economy. However, currently, the world’s major economies are modifying their frameworks of production policies from unsustainable to more sustainable, ecofriendly, and resource-conserving (Rhozyel and Zalpyt, 2018).

3. Lignocellulose biomass

3.1. Sources and production statistics

In the last decades, the use of fossil fuels has caused side effects on the environment, such as air pollution and greenhouse gas emissions resulting in global warming. As a result, intensive research for alternative biofuels or biomaterials derived from renewable sources with sustainable impact, has been undergoing (Ghimire et al., 2021; Okolie et al., 2021). As illustrated in Fig. 1, lignocellulosic biomass is a strategic natural renewable resource generated by different sectors such as agriculture, forestry, and industry. The demand for this resource has been increased over the past years.

The main high-value-added products from lignocellulosic biomass includes biofuels, biogas, biopolymers, and construction materials (Ciesielski et al., 2020; Devi et al., 2022). Only in 2019, 159 billion liters of biofuels were produced worldwide, with 70% of the total production in the Americas (WBA, 2021). Fig. 2 illustrates the biofuel production and world distribution. Among the productive sectors, the largest
amount of lignocellulose comes from woody biomass, agricultural residues (rice straws, corn stover, sugarcane bagasse), energy crops (switchgrass, miscanthus), cellulosic wastes (municipal solid waste such as pulp mill and lumber mill wastes) (Armah et al., 2022).

The world’s forests contain about 606 gigatons of living biomass (above- and below-ground) and 59 gigatons of dead wood (FAO, 2021). It generates nearly 1.3 billion tons per year of lignocellulosic biomass in the world (Fig. 2a). Among these biomass sources, rice straw is a sub-product of rice with global production of 370–520 million tons/year (Areepak et al., 2022). Sugarcane produces about 279 million metric
tons of bagasse, a source of lignocellulose biomass. Brazil is one of the largest producers at about 739,300 thousand metric tons per year, followed by other big countries such as India, China, and the United States (Ajila et al., 2021). The global production of corn stover is around 1 billion tons. Due to its high carbohydrate content, it is considered as an important feedstock for biofuel production such as ethanol (Ruan et al., 2019). In paper manufacturing, around 40 million tons of solid waste are produced per year. In this waste sludge, there are raw lignocellulosic materials that can be used for biorefinery applications (Zambare and Christopher, 2020). The residues from the pulp and paper mill biomass present a rich composition being a source of valuable materials such as black liquor (source of lignin and xylen), woody residues (source of cellulose), and fly ash (source of different minerals) (Haque et al., 2021).

The use of lignocellulosic residues is thought to reduce the dependency on petrochemical resources in fuels and plastic production. It is esteemed that more than 30% of fossil fuel replacement in the next years for biofuels, biochemicals, and biomaterials (Okolie et al., 2021) (Fig. 2 b, c). The use of lignocellulosic feedstocks provided by the agricultural and forestry sectors has great potential as an alternative to petrochemical resources, by this way it mitigates climate change and promotes economic development (Okolie et al., 2021). But, for an effective potential application of the compounds extracted from lignocellulosic biomass (lignin, hemicellulose, cellulose, and other extracts) must be fractionated into valuable forms (biofuels and/or chemicals) (Achinivu et al., 2021; Lobato-Peralta et al., 2021).

### 3.2. Isolation processes and physicochemical characteristics

Lignocellulose biomass (LCB) is made up of a variety of constituents, including cellulose, hemicellulose, lignin, pectin, and protein, as well as extractives (tannins, lipids, resins, steroids, terpenes, terpenoids, flavonoids, and phenolic compounds) (Haldar and Purkait, 2021; Okolie et al., 2021). LCB is a renewable source of carbon-neutral materials that can be used to produce biofuel and other intermediate products (valuables forms (biofuels and/or chemicals)). Although the composition of lignocellulose varies depending on the source, it typically consists of 40–60% cellulose, 20–40% hemicellulose, and 10–24% lignin (K N et al., 2022; Putro et al., 2016).

Cellulose is a polysaccharide composed of glucose units, linked by (β-1-4) glycosidic linkages. Hemicelluloses comprise a family of complex polysaccharides sharing with cellulose a backbone of (β-1-4) glycosidic linkages but are substituted and built by a wide variety of monosaccharides (glucose, xylose, galactose, fucose, mannose, etc., (Geng et al., 2019)). Lignin is a three-dimensional intricate complex aromatic heteropolymer composed of hydroxphenyl, syringyl, and, guaiacyl units that can variate in their ratios (Woiciechowski et al., 2020). These compounds change their composition according to the biomass source, origin, and climate conditions ( Wu et al., 2022). The lignin polymer network is a complex structure that acts as a physical barrier to access cellulose and hemicellulose (Mankar et al., 2021). The presence of lignin renders the biomass resistant to deconstruction since it is hardly depolymerized by enzymatic processes, which delays the extraction of cellulose and hemicellulose and becomes one of the major hurdles for large-scale commercial applications (Achinivu et al., 2021). The pretreatment of lignocellulose biomass is an essential step for uncovering the cellulose and hemicellulose for hydrolyzing process using enzymatic or chemical methods (Bhatia et al., 2020). Pretreatment allows the opening of compact structures in the plant cell walls permitting the contact of enzymes with cellulose and hemicellulose. In the absence of any pretreatment, the enzymatic hydrolysis activity can be as low as 20% (Liu et al., 2018). The pretreatment process is classified as physical, chemical, physicochemical, and biological, and it accounts for 40% of the total cost of the biorefinery process (Haldar and Purkait, 2021).

Some pretreatments, for instance, alkaline hydrogen peroxide, steam explosion, and organic solvents are used for extracting lignocellulose compounds. However, many of these pretreatments have side effects, such as the presence of various inhibitors of microbial activity, that can reduce some applications due to toxic effects (Wu et al., 2022). Furthermore, new methodologies for lignocellulose extraction have been developed as ammonia fiber explosion, hydrothermal treatments such as pressurized hot-water extraction (also known as subcritical water), supercritical fluids, co-solvent enhanced lignocellulosic fractionation, ultrasounds, microwaves, and deep eutectic solvents (Fig. 3) (Mankar et al., 2021). For example, in the lignocellulose conversion to biofuel, several thermochemical conversion technologies have been applied as pyrolysis, liquefaction, torrefaction, carbonization, and gasification, as well as biochemical conversion as digestion and fermentation (Okolie et al., 2021). Pyrolysis has been a highlight among the methodologies because of the flexibility to produce solid, liquid, and gaseous products from biomass. These processes have been classified as slow, fast, and flash pyrolysis, and the differences between the methods are the temperature and the residence time. However other parameters such as reaction conditions, reactor model, and catalyst addition among others change the final product (K N et al., 2022). Catalytic reductive depolymerization/fractionation (RCF) of lignin has recently emerged as one of the effective biorefinery approaches that combine lignin depolymerization with biomass. RCF uses a heterogenous catalyst system that prevents the depolymerization of lignin monomers yielding low molecular weight lignin-based monophenolics along with carbohydrate pulp (Liu et al., 2020). Briefly, the RCF biorefinery of lignocellulose is carried out in a high-pressure batch reactor (180–250 °C, 2–6 h). Heating stimulates the solvolytic extraction of lignin from lignocellulose biomass. Then the partial depolymerization of lignin starts by cleaving the ether bonds (like β-O–4 linkage) (Renders et al., 2019). The initial defragmentation yields unstable reactive fragments with a high tendency for repolymerization. These unsaturated fragments are stabilized through reductive redox-active catalysts such as Pd/C, which breaks the residual ether linkages (via hydrogenolysis). These phenolic units can be further deoxygenated to benzene derivatives using an appropriate catalyst. RCF can be categorized into a) solvent-free hydroconversion, b) hydroconversion in inert solvents, c) hydroconversion in hydrogen-donating solvent systems, d) and catalysis. A comprehensive discussion of categories can be found elsewhere (Bourbiaux et al., 2021).

Ultrasonication, irradiation, and microwave are techniques that have high efficacy for lignocellulose extraction from different types of biomasses. But the main challenge for the application of these methodologies is the demand for high energy inputs which increases the process costs (Haldar and Purkait, 2021). For lignin purification, fourtreatments have been used by the industry, including sulfite, Kraft, soda, and organosolv pretreatments. Between these methodologies, the organosolv fractionation showed a promisor technique for biomass fractionation once it demonstrated low side-effects on the environment, great delignification efficiency, and the production of several sub-products (Achinivu et al., 2021). From the extraction of lignocellulose biomass, several products with industrial applications can be obtained. For example, the production of biodiesel and biogasoline, chemicals such as ethanol, phenols, aldehydes, xylitol, and saccharides with low carbon emission (Baruah et al., 2018).

Lignocellulose is a great alternative for substitute petrochemical products; however, many challenges must be overcome. Green methodologies must be a priority for industrial processes, however, these technologies for biomass extraction still need to be improved for the scale-up process. The high costs for industrial infrastructure and methodologies that have high extraction efficacy with a low-cost process are the main challenge to their application (Haldar and Purkait, 2021).

### 3.3. Transformation processes

The fractionated lignocellulosic polymers – cellulose, hemicelluloses, and lignin – can be functionalized and chemically modified to fine-tune their properties and expand their applications into a range of bioproducts. In the case of cellulose extracted from agricultural
lignocellulosic side streams, such functionalization processes have traditionally been carried out in bulk, yielding cellulose derivatives similar to those obtained from wood-derived sources (Heinze and Glasser, 1998), such as carboxymethyl cellulose or cellulose acetate (Biswas et al., 2006). Such bulk chemical modification procedures usually require solubilization of the cellulose and disrupt the native organization of the cellulose microfibrils, therefore resulting in a loss of their structural properties. In recent years, the focus has been placed on the surface modification of cellulose fibers to preserve their structural integrity and enable at the same time surface functionalization of the fibers towards desired properties such as hydrophobicity, ionic stability, or even bioactivity (e.g., antimicrobial properties) (Kamel et al., 2020). Common procedures for the surface modification of cellulose fibers from agricultural sources include esterification reactions (i.e., acetylation (Kellersztein and Dotan, 2016), propionylation (Singh et al., 2016), succinylation (Leszczyńska et al., 2019), etc.), resulting in functionalized cellulose fibers with different degrees of substitution and chemistries of the introduced agents, thus balancing the hydrophilic/hydrophobic properties of the fibers (Fig. 4). TEMPO-mediated oxidation is now a well-established methodology for the preparation of cellulose nanofibers from lignocellulosic streams including crops such as bast of flax, hemp, jute, leaves of sisal and abaca (Alila et al., 2013), wheat straw (Miao et al., 2020) resulting in the introduction of carboxylic groups in the fiber surface. These anionic moieties contribute to the colloidal stability of the cellulose fibers (Mendoza et al., 2018) and can be further exploited for the introduction of other functional groups (e.g., through amidation) and even the grafting of polymeric chains from the cellulose surfaces (Heise et al., 2021). Kaldeus et al. (2019) reported the synthesis of polymers and copolymers of poly(ethylene glycol) methyl ether methacrylate (POEGMA) and poly(methyl methacrylate) (PMMA) from cellulose nanofibril by introducing surface activators.

Hemicellulose constitutes a widely abundant fraction in agricultural

---

Fig. 3. Routs towards isolation of different components, i.e., cellulose, lignin, and hemicellulose from lignocellulosic biomass.

Fig. 4. Surface modification of cellulose fibrils by TEMPO-mediated oxidation, esterification, and grafting from approaches.
side streams, but they, unfortunately, remain an unexploited resource in lignocellulosic biorefineries from crops. Due to the higher solubility of hemicelluloses, their chemical modification and functionalization are usually performed in the bulk. The rich palette of carbohydrate chemistry offers broad possibilities for the modification of the hydroxyl groups in hemicelluloses, by oxidation, esterification (acetylation, succinylation, benzylation), etherification (carboxymethyl, methylation, hydroxylalkylation, benzylation), grafting from, grafting too, and cross-linking. (Chen et al., 2015; Soderqvist Lindblad and Albertsson, 2004).

These chemical procedures enable the fine-tuning of the physicochemical properties of the hemicelluloses from agricultural side streams (Huang et al., 2021) towards increased hydrophobicity for water-sensitive applications and (Farhat et al., 2017) film-forming properties (Hansen and Plackett, 2008; Zhao et al., 2020). In particular, thermoplastic hemicelluloses can be prepared by ring-opening graft polymerization using caprolactone as the monomer (Farhat et al., 2018), or oxidation and further etherification (Borjesson et al., 2019; Deralia et al., 2021) of the side chains. These introduced chemical moieties act as internal plasticizers of the modified hemicelluloses, increasing the thermal processability, rheological properties, and thermo-mechanical properties of the derived materials. In agricultural side streams, hemicelluloses are natively covalently bound to hydroxyycinnamic acids such as ferulic acid, which confer the hemicellulosic chains with important bioactivities such as radical scavenging, antioxidant, and antibacterial properties (Ruthes et al., 2017). These feruloylated hemicelluloses can be used as matrices for the preparation of antioxidant films or hydrogels (Niño-Medina et al., 2016; Yilmaz-Turan et al., 2020), with potential applications as active food packaging and biomedical devices.

In parallel to the chemical modification of lignocellulosic polymers from agricultural resources, enzymes can be applied to fine-tune the substitutions of hemicelluloses and even to introduce new functionalities in the polymeric chains (Martínez-Abad et al., 2016; Vuong and Master, 2022). The use of enzymatic catalysis instead of chemical catalysis has a lower environmental fingerprint, as these procedures can be performed at low temperatures and in aqueous conditions, avoiding the use of hazardous chemicals (Hauer, 2020). The fine structure of arabinoxylan from agricultural resources, the degree of substitution, and the molecular weight can be adjusted by different glycosyl hydrolases (e.g., arabinoxylanoxidases and xylanases, respectively), which have a large influence on the material properties of the resulting films (Hoije et al., 2008; Sternemalm et al., 2008). Oxidative enzymes, such as galactose oxidases, can be used to regioselectively introduce carbonyl groups in the hemicellulose structures (Parikka et al., 2010), which enable the preparation of hydrogels and aerogels with improved rheological and mechanical properties (Mikkonen et al., 2014; Parikka et al., 2012). These oxidized hemicelluloses can be further modified chemo-enzymatically to expand the range of functional groups (e.g., amino groups, click functionalities) toward advanced structural and biomedical applications (Aumala et al., 2019; Xu et al., 2012). Other oxidative enzymes, such as lytic polysaccharide monoxygenases (LPMOs), are capable of oxidizing the surface of crystalline cellulose fibrils introducing carboxylic acids in a regioselective manner without compromising the mechanical integrity of the fibers, therefore promoting the preparation of cellulose nanofibers and nanocrystals (Karnouzi et al., 2020; Koskela et al., 2021). Oxidoreductase enzymes, such as laccase and peroxidases, can be used for the covalent crosslinking of feruloylated arabinoxylans derived from cereal sources, thus enabling the preparation of polymeric hydrogels with large potential in food and biomedical applications (Munk et al., 2020; Yilmaz-Turan et al., 2022; Zhang, X. et al., 2019a,b). As discussed earlier, lignin is the second most abundant natural polymer and the only industrially viable/renewable feed stock rich in aromatic monomers. Chemically lignin is an amorphous polymer comprised of three major phenylpropanolic monomers (monolignols) that are linked via carbon and ether bonds. However, it still ranks as the most underutilized feedstock in the bioproduct industry (Ha et al., 2019). Lignin can be converted into an array of useful chemicals replacing petroleum-based feedstock through different conversion approaches including gasification, pyrolysis, hydrocracking, acid or alkali hydrolysis, and catalytic reductive and oxidative transformation. Additionally, a recently developed approach known as the lignin first approach has been utilized to convert lignin into valuable chemicals (Jing et al., 2020).

Due to its high phenolic component concentration, lignin pyrolysis oil is a prospective source for the synthesis of useful chemicals; however, due to its high oxygen levels, viscosity, and instability, catalytic pyrolysis, and additional catalytic upgrading are being explored. The catalytic pyrolysis of lignin has been utilized to produce value-added stable compounds using a variety of catalysts, such as zeolites (Ben and Raguasus, 2012), metal oxide (Mullen and Boateng, 2010), spent fluid catalytic cracking (FCC) catalyst, alumina (Bouisin et al., 2015), metal chlorides (Zhu et al., 2019), and mesoporous materials (Wang, S. et al., 2022a,b). As per reports, elevated temperatures and catalyst contents (catalyst-to-lignin ratio) can result in higher aromatic hydrocarbons. Higher temperature helps in opening the catalytic pores, and an increase in catalyst leads to the growth of the overall acid sites. Hydrodeoxygenation of lignin pyrolysis oil (LPO) is considered as the most efficient route to convert LPO into deoxygenated biofuels and other valuable chemical products. Briefly, the oxygen from aromatic rings of LPO has been removed in the presence of hydrogen and metal catalyst. The removal of oxygen from methoxy and hydroxyl group is carried out in the form of water and methanol (Cesari et al., 2019).

4. Circular economy and a new perspective for lignocellulose biomass use

4.1. Biofuels

4.1.1. Overview of biofuels

The environmental impacts of climate change associated with the tendency to reduce dependence on fossil fuels boosted contemporary society’s search for renewable sources. Countries have played a leading role in this process, especially China, India, the United States, Brazil, and the European Union (OECD, and FAO, 2021). In the European Union (EU), the share of renewable energy in the final gross consumption of its Member States reached 22% in 2020, with its target of 32% by 2030. However, some sectors still depend significantly on petroleum-derived fuels as the European transport system, as 92% of energy consumption was from fossil sources in 2017 (EEA, 2022). For this reason, one of the European community’s strategies to reduce greenhouse gas (GHG) emissions is to eliminate and replace fossil fuels with energy from renewable sources by 2050 (Popp et al., 2021). In Brazil, the Renovabio Law established a 10% reduction in GHG emissions in the fuel sector by 2028 (OECD, and FAO, 2021). In that country, the proportion of anhydrous alcohol mixed with gasoline reaches 27%, and the biodiesel mixture coefficient is 11%. In 2021, around 88% of 1.6 million new cars licensed in Brazil were flex-fuel (gasoline and ethanol) (ANFAVEA, 2022). The United States and China adopt a 10% blend of ethanol in the fossil fuel used by the transport sector (OECD, and FAO, 2021).

This scenario boosted the production of first-generation biofuels (1G) such as ethanol, biodiesel, and biogas due to their renewable character (AliAkbari et al., 2021). In 2019, the global production of biofuels reached 159 billion L, especially ethanol and biodiesel. The United States (48.2%) and Brazil (26.7%) accounted for around 75% of the global production of 1G ethanol (total of 115 billion L), while the EU (22.3%) and the United States (18.1%) produced 50% of global biodiesel (total of 41 billion L) (OECD, and FAO, 2021). Global biogas production totaled 62.3 billion m³ (or 1.43 EJ), with an annual growth rate of 9% from 2000 to 2019 (WBA, 2021). Europe stood out, producing 30.6 billion m³ of biogas, or about 50% of the global total, with energy equivalent to 0.70 EJ in 2019 (WBA, 2021).
The production of 1G ethanol is mostly from starch (corn, potatoes, and tubers) (59%) and sugar (sugarcane, beets, and fruits) (24%), while about 73% of biodiesel is based on vegetable oils (14% rapeseed, 24% soy, and 31% palm) or used cooking oils (20%) (OECD, and FAO, 2021). This feature emerged in a debate related to the competition between crops for food production versus energy (Jain et al., 2022). In this context, EU Directive 2015/1513 set a maximum of 7% of biofuels derived from cereals, starch, sugars, and oilseeds by 2020 (including those grown for energy on agricultural land) for the transport sector (Hassan et al., 2019). The debate on producing food versus fuel as a raw material potentiated the alternative of LCB, from agro-waste, as a raw material for 2nd generation (2G) biofuels, especially in developed countries (Kapoor et al., 2020). The EU aims to get 25% of its energy from the transport sector through second-generation biofuels (Hassan et al., 2019). In the United States, the Energy Policy Act of 2005, published as the Renewable Fuels Standard (RFS), had the main objectives to increase biofuel production to 136 billion L by 2022 and encourage the production of 2G ethanol (Banu et al., 2021). Therefore, 2G biofuels using LCB add value to forest, agricultural, urban, and industrial waste, promoting the circular economy, reducing GHG emissions, and contributing to solid waste management in contemporary society.

4.1.2. Second-generation biofuels

Lignocellulosic biomass is one of the best alternative substrates to produce biofuels and an excellent substitute for first-generation raw materials due to its abundance and availability, being a low-cost renewable resource, and allowing the recovery of waste, promoting the circular economy (Devi et al., 2022; Wang and Lee, 2021). Therefore, 2G ethanol produced from LCB is an exciting energy alternative, especially for countries that generate a significant amount of agricultural and forestry waste, such as Brazil, China, India, and the United States (Devi et al., 2022).

Cellulose and hemicellulose, present in LCB, are raw materials for second-generation biofuels. As a valued raw material, the global market projects the growth of cellulose fiber from US$21.5 billion in 2017 to US$41.5 billion by 2025 (Banu et al., 2021). Despite high availability, there is no straightforward process to convert lignocellulosic biomass into biofuel. Furthermore, the recalcitrant effect of lignin, the third component of LCB, affects biofuel processes by introducing a pre-treatment step to degrade lignocellulosic material (Velvizhi et al., 2022). The pre-treatment step is essential, as it brings about several changes in the biomass and directly influences the sugar conversion efficiency (Liu et al., 2021). Therefore, a series of processes are required for bioconversion, from pre-treatment to hydrolyze cellulose and hemicellulose.

Fig. 5. The circular economy approach in biofuels and other side streams from lignocellulosic biomass (Hernández-Beltrán et al., 2019).
into their fermentable sugars, fermentation, and finally, the distillation of the fermented broth (Liu et al., 2021). Two pathways for converting LCB into biofuels are highlighted: thermochemical conversion and biological conversion (Chintagunta et al., 2021) (Fig. 5). In thermochemical conversion, raw materials-controlled heating or oxidation generate energy products, especially pyrolysis, and gasification (Kapoor et al., 2020; Rodionova et al., 2021). The pyrolysis of biomass produces solid (biochar), gaseous (CO2, CO, CH4, H2), and liquid (bio-oil), which is further processing produce methanol, ethanol, biohydrogen (Devi et al., 2022; Rodionova et al., 2021). The biological conversion (bioconversion) from LCB is possible to produce liquid (ethanol and biobutanol, biodiesel) (Uthandi et al., 2022; Wang and Lee, 2021) and gaseous biofuels (biomethane and biohydrogen) (Banu et al., 2021; Kapoor et al., 2020).

Biological conversion is the most common method to produce ethanol compared to thermochemical conversion due to its high conversion efficiency and selectivity (Wang and Lee, 2021). This conversion pathway of converting LCB into ethanol also includes the pre-treatment phase, followed by enzymatic hydrolysis and the fermentation of sugars (Kapoor et al., 2020). Fermentation organisms capable of C5 metabolism consist of yeasts (e.g., Saccharomyces cerevisiae, Pichia stipitis etc.) and bacteria (Zymomonas mobilis, Clostridium thermocellum etc.) (Wang and Lee, 2021). Biobutanol can be used as a biofuel or gasoline additive and has several advantages over ethanol, such as lower volatility, higher energy content, energy density, and net heat capacity. Furthermore, the air/fuel ratio and energy content of butanol are close to gasoline (Wang and Lee, 2021). Various agricultural residues (grass, corn straw, wheat straw, sugarcane bagasse) are feedstock to produce biobutanol, in which different species of clostridium i.e., Clostridium acetobutylicum, Clostridium beijerinckii, and Clostridium tyrobutyricum act as fermenting organisms. However, the lignocellulosic biomass substrate must be composed of a high percentage of cellulose and hemicellulose and a low percentage of lignin due to the recalcitrant effect of the polymer (Koul et al., 2022).

Biodiesel is a renewable and biodegradable liquid fuel that substitutes petroleum-derived diesel in the transport sector (Uthandi et al., 2022). Restrictions on the production of first-generation biodiesel have boosted second and third-generation biodiesel, obtained from inedible oils (used cooking oil), oils from plants that grow on land unsuitable for agriculture, or microbial oils (López-Fernández et al., 2021). LCB is a feedstock to produce biodiesel from agricultural waste such as rice bran, inedible oilseeds, coffee grounds, and oil-free cakes because they contain residual oil (Koul et al., 2022). Another way researched refers to the use of LCB as a substrate for oleaginous microorganisms (OMs) to produce lipids (Koul et al., 2022; Uthandi et al., 2022). When cultivated under specific environmental conditions, these microorganisms can accumulate 20–70% of oils inside their cells (Uthandi et al., 2022). Furthermore, OMs could enhance the circular economy and cost-effective process development (Chintagunta et al., 2021). Following the trend observed in other second-generation liquid biofuels, pre-treatment of LCB is necessary to release lignin and make cellulose more accessible to enzymatic hydrolysis, fermentation with OMs to produce lipids, and subsequent transesterification of lipids into biodiesel (Uthandi et al., 2022; Vassaki et al., 2022). In the production of gaseous biofuels, LCB can be treated by anaerobic digestion (Ghimire et al., 2021). Biomethane, one of the leading gases generated in the anaerobic digestion process, is an alternative for the transport sector or can be injected into the national gas distribution network (Banu et al., 2021; Wang and Lee, 2021). However, the recalcitrance of LCB to biodegradation requires a pre-treatment to facilitate the degradation of lignocellulosic materials during anaerobic digestion (Khan et al., 2022). These authors reviewed the main physical pre-treatments (mechanical, extrusion, irradiation), thermochemical (hot water, stem Explosion), chemical (alkali, acidic, organosolv), oxidative (wet oxidation, advanced wet explosion, ozonolysis), biological (fungus, microbial consortium, enzyme), and hybridge pre-treatment for the use of LCB in anaerobic digestion.

Another gaseous biofuel highlighted in the literature is biohydrogen, which corresponds to hydrogen produced via biocconversion and is considered a green and clean biofuel. Biohydrogen is a potential alternative to fossil fuels due to its high gravimetric-based energy content and absence of greenhouse gas emissions after combustion or oxidation, in addition to the possibility of being mixed with natural gas. The primary raw material for hydrogen production is corn stalks (Medina-Morales et al., 2021). Following the trend of biomethane production, pre-treatment techniques have been developed to improve the performance of the bioconversion process (Khan et al., 2022; Liu et al., 2021).

4.1.3. Barriers and challenges to the use of LCB in the production of biofuels

2G biofuels have the potential to replace fossil fuels due to the possibility of using waste from different sources, promoting the circular economy. However, barriers and challenges emerge to the growth of its production on a commercial scale, as advanced biofuels supply less than 1% of biofuels (IRENA, 2019). Investments by the EU and the United States to stimulate the use of various lignocellulosic feedstocks have not impacted the production of 2G biofuels, as desired. The global advanced biofuels industry is still small, as only 12 refineries reached an annual production capacity of more than 10 million L of 2G ethanol at a commercial level in 2018 (IRENA, 2019). Advanced biofuels are subject to numerous technological, infrastructure, economic, environmental, social, and political barriers, reflecting the complex nature of the business environment (IRENA, 2019). This picture can be gauged by some economic indicators, such as the cost of biomass, which varies from US$ 22 to US$ 85 per ton, depending on its variability and accessibility (Devi et al., 2022). Another economic indicator refers to the specific investment cost per annual production capacity, which reaches US$ 45 per L for 2G ethanol and only US$ 0.5–0.6 per L for conventional ethanol (IRENA, 2019). A compilation of the reviewed literature presents the barriers and challenges to the growth of LCB-based 2G biofuel production (Fig. 6).

4.1.3.1. Planting and collection of lignocellulosic biomasses. The first question refers to the source of LCB that should be obtained from agricultural residues, agro-industrial processes, and the urban solid residue collection system. Crops as a source of LCB should be restricted to those grown in degraded areas (Jatropha, Makauba) or unsuitable for food crops (Banu et al., 2021; López-Fernández et al., 2021). However, agricultural waste has a limited ability to meet society’s demand for fossil fuel replacement. Holmatov et al. (2021) estimated the global potential for 2G ethanol production based on 123 crop residues generated in 192 countries and 20 territories. In the optimistic scenario, the availability of residues (generated in the field during harvest and at processing sites) to produce 2G ethanol was 50%. The total annual potential of net 2G ethanol production in this scenario would allow 13% of global oil consumption in the transport sector to be replaced in 2017 (Holmatov et al., 2021).

The use of agricultural residues generated in the harvesting process demands the promotion of technologies for the in-situ management and recovery of these residues for industrial applications, such as agricultural machinery for collection, drying, densification, baling, and transport (Kapoor et al., 2020). However, the importance of agricultural residues in nutrient cycling and soil protection against water erosion, an issue especially important in tropical and subtropical regions, due to torrential rains, should be highlighted. Important grain-producing regions, such as the Brazilian Cerrado, develop production systems based on maintaining high soil organic matter, such as the crop-livestock-forest system (Costa et al., 2018).

4.1.3.2. Logistics. The logistics sector to meet the supply of LCB to the industrial sector involves the steps of collection, drying, densification
transport, and storage, which vary depending on the type and source of LCB (Hassan et al., 2019). These authors highlighted aspects such as the geographic decentralization of LCB generating sources, the seasonality of the supply, the variability of the moisture content, the density of the raw material and its contamination, proximity of the LCB generating area concerning the biorefinery and availability of facilities for storage. The infrastructure of roads, railways, and ports should be added. These issues are potentiated in emerging countries, such as Brazil, due to its continental dimensions and contrast of logistical structure in the territory (Mancini et al., 2021), and in the African continent (Cristovão et al., 2021).

4.1.3.3. Research and technological development. Technological advances, new industrial methods, and new infrastructures in agribusiness are guidelines highlighted by several researchers to improve the productive and economic performance of the production of 2G biofuels (Melendez et al., 2022; Sherwood, 2020). Regardless of the type of 2G biofuel to be produced, or the LCB conversion route (thermochemical or biological), pre-treatment is seen as a step that raises production costs, requiring the development of more economically viable and sustainable techniques (Khan et al., 2022; Wang and Lee, 2021). In the way of thermochemical conversion of LCB into 2G biofuels, the low quality and high acidity of the bio-oil are the main limitations for the use of bio-oil obtained from the pyrolysis of biomass, requiring the upgrade by hydrodeoxygenation (Wang and Lee, 2021). In the LCB biological conversion pathway, the main recommendations refer to genetic manipulation and metabolic engineering for the development of microorganisms and enzymes (Kapoor et al., 2020; Liu et al., 2021). In the conversion of cellulose into biofuel, the pre-treatment of LCB is followed by the enzymatic breakdown and its conversion into ethanol, allowing us to foresee a considerable future demand for cellulase enzymes (Devi et al., 2022; Kapoor et al., 2020). The genetic engineering of oleaginous microorganisms (OMs) associated with the process of bioconversion of LCB as a substrate in the production of biodiesel would reduce the cost of the processes and increase their efficiency (Chintagunta et al., 2021; Uthandi et al., 2022). Sherwood (2020) indicates other areas for the development of anaerobic digestion of LCB, such as reactor designs and technology for process monitoring and control. Devi et al. (2022) indicate strategies for co-production, reuse of LCB to maximize the use of resources and aggregation of value in the waste generated during the process.

4.1.3.4. Circular economy policies. Sustainability is a global polical objective, the Sustainable Development Goals (SDG) promote a global framework aiming for environmental protection, reducing climatic change effects, promote quality of life, among others (Ziegler et al., 2023). There are government initiatives to implement affordable policies to encourage the circular economy. The desire of the European Union (EU) Green Deal to restructure industrial sectors to promote the circular economy, to minimize negative environmental impacts on the issue of production and consumption (Lukkarinen et al., 2023).

An important role for governments is the creation of new bioresource policies that encourage technological, socioeconomic, and institutional innovations for a circular economy (Kapoor et al., 2020). There are institutional challenges that refer to the standards evaluation, laws, and rules, to recycling procedures to obtain new products with high quality. With this situation, there are challenges regarding tax laws relating to recycled products. This unclear scenario creates financial barriers regarding economic costs in the circular economy implementation systems in the agri-food sector (Abbate et al., 2023).

4.1.3.5. Government and market policies. The biofuels sector, 2G, is influenced by the market environment. Therefore, the government can promote the growth of the sector, through economic policies and incentives. In 2020, the COVID-19 pandemic caused an 8.5% drop in the global use of transport fuels, compared to 2019, causing an 8.7% reduction in the use of biofuels due to restrictions on the movement of people and disruptions in commercial logistics across the planet (OECD, and FAO, 2021). During this period, the production of biofuels was affected by the rise in commodity prices, such as corn and vegetable oils, associated with the fall in fossil fuel prices. However, government support has eased some of the pressure on markets, in addition to the growing use of ethanol in the industry as a disinfectant during the pandemic, allowing the production of biofuels to be sustained (OECD, and FAO, 2021). An important government role to promote the growth of the biofuels chain is to provide adequate infrastructure, including port facilities and roads, to connect feedstock producers and biorefineries, in addition to tax cuts and subsidies offered to biofuel producers, mandatory regulation, application mechanisms, and investment in non-traditional raw materials for the production of biofuels, such as LCB (Melendez et al., 2022; OECD, and FAO, 2021).

(Sherwood, 2020) argued that the duration of a sustainable biomass production certificate can last up to 5 years, like the Forest Stewardship Council (FSC) certification for forestry. This author suggests that a greater requirement for biomass producers to sustainably manage land use over a longer period would promote the circular economy. The
competitiveness of the production and commercialization of biofuels, especially the production of 2G, concerning fossil fuels, which have a much longer period of development and maturation of processes, should not be reversed in the near future. However, energy systems aimed at the transport sector and based on biomass are one of the main solutions for a sustainable and low-carbon society. The integration of processes, the recovery of generated waste, and the development of other value-added products should enable biorefineries to produce biofuels based on lignocellulosic biomass.

4.2. Bioplastics

Bioplastics are the ones that are biodegradable and/or are made from renewable sources (Fredi and Dorigato, 2021; Kawaguchi et al., 2022), as can be seen in Fig. 7. The production of bioplastics reached 2.1 million tons in 2020 (Fredi and Dorigato, 2021), while the total plastic production was 367 million tons in the same year (Plastics Europe, 2021). However, the raw material and microbial process costs and the need for purification for later polymerization hinder the competition between bioplastics and petrochemical plastics. Even so, it is possible to produce traditional polymers bio-based, such as biopolyethylene and biopropylene, which use natural raw materials, and the bioPET –polyethylene terephthalate, which usually has only one of its raw materials from natural sources (Fredi and Dorigato, 2021; Jorda et al., 2019). Consumers of these green versions are willing to pay a higher price for materials with lower environmental impact, mainly greenhouse gas emissions (Prasanth et al., 2021). However, besides cost, this option has other issues, including environmental problems: 1) these plastics present properties similar to the petrochemical ones, i.e., they are not biodegradable, and if their waste were not conveniently treated, they can end up in landfills or even in streets, rivers and ocean, where they can probably generate microplastics during the time (Garcia-Depract et al., 2021; Ita-Nagy et al., 2020), 2) they are usually produced with edible raw material, such as sugars that can be converted to bioethanol by fermentation (and this in ethylene and polyethylene, for instance) (Kawaguchi et al., 2022). These aspects raise discussions such as the use of a great deal of land to produce plastics (and not food) that can be transformed into one-way products and bring the already cited problems when they become waste (Escobar and Britz, 2021; Ita-Nagy et al., 2020).

In contrast, polymers usually employed in more demanding and/or long-life applications can be bio-based, such as polymethylmethacrylate, polyurethanes, and polyamides. They can be partially produced with by-products of itaconic acid, industrially obtained from glucose fermentation. Efforts have been made to produce this acid from other lignocellulosic biomasses, such as beech wood, bamboo, corn stover, wheat bran, and wheat chaff, to reduce the cost of obtaining it by 50%. However, obtaining fermentable sugars from lignocellulosic materials is still expensive (Kawaguchi et al., 2022). For instance, only 0.3% of the worldwide bioethanol production in 2017 was second-generation bioethanol, produced with agricultural waste mainly in Europe, China, and the United States. There is no information on the percentage of this bioethanol used to produce bioplastics, even bio-based versions of traditional plastics such as polyethylene and polypropylene (Mendieta et al., 2020). Forest waste (e.g., Pinus), agro-industrial waste (such as the paper industry), or even food waste (such as bread waste) can also produce bioethanol (Narisetty et al., 2021; Suvachan et al., 2021).

The employment of lignocellulosic biomasses from agricultural waste to produce bioplastics may probably bring a cost reduction and solve one of the related problems (no land would be used for this, leaving the land free for food production). Several non-edible sources have been investigated as lignocellulosic feedstock, such as apple pomace, banana peels, coconut fiber, coffee husks, corn stover, corn cob, grape pomace, mango peels and stones, pineapple leaf, rice husk, rice straw, spent coffee grounds, sugarcane bagasse and wheat straw (Lu et al., 2022; Otoni et al., 2021). Using these raw materials to obtain biodegradable plastics could diminish the waste problem, although some discussions can and will be raised on this aspect (Goel et al., 2021; Kawaguchi et al., 2022). In addition, biodegradable plastics usually have some final properties lower than the ones presented by traditional petrochemical plastics, hampering their employment as an alternative.

![Fig. 7. Classification of bioplastics. Some bioplastics can also present both raw materials (biobased and petroleum-based). Agricultural wastes can produce a variety of bio-based plastics (biodegradable or not).](image-url)
and the establishment of a circular economy based on non-edible LCB (Otoni et al., 2023; Prasanth et al., 2021). It is a fact that the aromatic nature of lignin attracts researchers who aim to optimize its use as reinforcement in polymeric molecules in the form of blends with other polymers (normally bio-based) or new bio-based polymers, such as cinnamate-based polyesters, truxillic acid-based polyimides, bio-based polybenzoxazoles, and itaconic acid polyamides (Kawaguchi et al., 2022; Mariana et al., 2021). Bio-based composites can also help achieve the goal of good performance and low cost: a techno-economic evaluation study revealed that a bio refinery producing lignin-based polyurethanes foams and cellulose-based biocomposites from wood barks would bring a return of the capital employed of 15.5% and 6.4 years of payback period (Ajao et al., 2021).

Despite difficulties, some biodegradable and bio-based polymers are available such as polylactic acid (PLA) and poly (butylene succinate) (PBS). PLA can be produced from bio-based lactic acid, and its global production reached 190 thousand tons in 2019 worldwide. PBS is chemically produced from 1,4-butanediol (petrochemical source) and bio-based succinic acid (Kawaguchi et al., 2022). Other common bioplastics are polyhydroxyalkanoates (PHAs), such as poly (3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV). They are produced and used as carbon and energy storage by some bacteria after the fermentation of available sugars. The higher price of the biodegradable and biobased polymers has stimulated research on waste, such as milk whey, used cooking oil, as well as rice straw, rice husks, corn stover, and even starchy wastewater, like the ones from the cassava processing industry (Chavan et al., 2021, 2022). As can be seen in Fig. 1, bioplastics can be petroleum-based since they are biodegradable, such as poly (butylene adipate-co-terephthalate) (PBAT) and poly caprolactone (PCL). Mainly PBAT is commercially available in an application that seems perfect for biodegradable plastics: biodegradable mulches (BDMs). After use, these films biodegrade, being incorporated into the soil and not hindering the next harvest. Therefore, researchers try to obtain BDMs from inedible biomass, such as orange peels and spinach stems (Merino et al., 2021).

The increasing production and diversity of bioplastics raise concerns about recycling these materials, especially the biodegradable, since the non-biodegradable ones are typically green versions of petrochemical ones and can be mixed with petroleum-based polymers in a recycling facility. The biodegradable plastics, produced from agricultural non-agricultural waste, must be separated from the rest of the plastics and from each other to make recycling feasible and high-quality. With this in mind, PLA, the most produced and discarded biodegradable plastic, must be the initial target of recycling streams only with biodegradable plastics (Fredi and Dorigato, 2021).

4.3. Lignocellulosic materials at nanoscale regime

Nanotechnology opens the door for a whole range of sustainable and renewable industrial lignocellosic biomaterials related to cellulose, lignin, starch, and other constituents at the nanoscale by exploiting wood and other plant biomass to impart greater functionalities. By utilizing the “quantum effect”, these nanometer-sized building blocks give rise to unique properties such as inherent strength (high specific Young’s modulus), large surface area, optical transparency, variable to low thermal expansion coefficient, flexible surface chemistry, nontoxicity and so on, to nano-enabled biomass-based products that can be easily applied to lignocellosic sensors, self-cleaning surfaces, electronic devices, pharmaceutical materials, etc., that have potential to replace the petroleum-based commodities (Lucia and Rojas, 2009). At this scale, it is interesting to probe the biomass for its nanstructures and composition by utilizing high-end characterization techniques, including various microscopy and spectroscopy, and analytical tools for measuring their properties at the nanoscale. The size of such nano entities is measured by microscopy techniques such as atomic force microscopy (AFM), and transmission electron microscopy (TEM), or it is deduced from small-angle neutron or X-ray scattering (SANS, SAXS, XRD) or by dynamic light scattering (DLS) reported as hydrodynamic radii (Beecher et al., 2009). Cellulose at the nanoscale is categorized depending on its sources and extraction processes into micro/nanofibrillated, nano-crystalline (nanowhiskers/ nanowires), and bacterial cellulose.

Fibrillated cellulose has nanostructured aggregates that exhibit crystalline and amorphous portions of length in the range of several micrometers with lateral dimensions within 3–100 nm, depending on the source, pretreatment (mechanical, enzymatic or acid hydrolysis, or oxidant-based) and further preparatory processes (Yu et al., 2021). Cellulose nanocrystals (CNC) are rigid rod-like particles with a typical needle-like structure that have monocrystalline domains of 1–100 nm in diameter and up to hundreds of nanometers in length. CNC of various dimensions extracted from different sources have been reported such as 100–1000 nm long and 10–50 nm wide from bacterial sources, 70–300 nm long and 5–10 nm wide from cotton; while 100–300 nm long and 3–5 nm wide from wood (Fortunati et al., 2016). The morphological characteristics of nanocellulose obtained from various biomass sources are shown in Fig. 8a-l.

CNC extracted from sea animals or tunicates have larger dimensions due to the presence of a greater number of crystalline domains compared to the amorphous regions. While the purification steps start with the removal of lignin and hemicellulose matrices followed by the homogenization process in the case of plant biomass sources, bacterial cellulose is formed utilizing biotechnological assembly of low-molecular-weight carbon sources excreted from the pores of Komagataeibacter bacterial cells, that are cultivated in common aqueous nutrient media. Hundreds of thousands of glucose molecules polymerize with the help of cellulose synthase enzyme behind the pores. This results in the formation of a bacterial cellulose nanofibre network with 20–100 nm diameter and several micrometers in length having mechanical stability and high crystallinity (Vadanan et al., 2022). The cellulose yield depends on various bioprocessing factors such as the type of growth medium, temperature, DO, pH, temperature, etc. The properties such as colloidal stability in polar solvents/water, size, and crystallinity index determine the quality and consistent performance of CNC. The particles are colloidally stable when they are well dispersed and resist aggregation or sedimentation in the solvent, and this property determines the viscosity, shelf life, and processing efficiency of CNC (Vanderfleet and Cranston, 2021).

Cellulose at the nanometer scale targets properties like aspect ratio and crystallinity index. While a high aspect ratio promotes the self-assembly of CNC into liquid crystalline phases that give rise to uniform and strong percolated networks giving robust interfaces, crystallinity influences its mechanical, chemical, and thermal characteristics (Lagerwall et al., 2014). Assembling nanocellulose fibrils into bulk microfibrils by various methods such as wet twisting/dry fixing and microfluidic spinning methods have shown remarkable enhancement in tensile strength (800 MPa and 1.6 GPa, respectively) and Young’s modulus (66 and 86 GPa, respectively) compared to conventional bulk cellulose paper (Guan et al., 2020; Li et al., 2021). Nanopaper made of nanocellulose assembled free-standing films or coatings on substrates with high packing density shows tremendous gas barrier performance, and its tunable porosity provides desired optical transmittance and thermal conductivity properties, making it an excellent material for packaging applications (Hsieh et al., 2017; Lin et al., 2019).

Lignin nanoparticles (LNP) are eco-friendly entities produced by chemical or physical methods from various sources and are finding their application as reinforcing and packaging materials, thermal or light stabilizers, dispersants, biocompatible and degradable materials, coatings, and adhesives. The chemical synthesis processes include anti-solvent precipitation using acids, water or supercritical CO2, self-assembly, aerosol flow synthesis, ice segregation-induced self-assembly, etc., while mechanical treatments utilize homogenizer, ultrasonic irradiation, etc (Luo et al., 2022). While the former can produce uniform (spherical, hollow, quasi-spherical), well-dispersed, and pH-stable
nano-lignin (shown in Fig. 8 m-p), the latter may give broad distribution ranging from large micron-to nano-sized particles. Its mechanical strength, UV shielding, antimicrobial, flame resistance, and antioxidant properties have been widely investigated, making it an excellent candidate for introducing functionalities to the polymer matrix while overcoming the disadvantages of inorganic nanomaterials with similar characteristics.

Several examples of nanocomposites, such as lignin-based-Ag⁺ ions, films of LNP/CH/PVA, LNP/CNC/PVA, and the composite of modified LNP with Cu and Zn have been tested for improved bactericidal properties for a range of pathogens (Richter et al., 2015; Yang et al., 2016). The polyphenolic structure and a high number of phenolic hydroxyl groups of spherical and colloidal LNPs synthesized from various sources have been used for increased UV absorption and antioxidant properties, paired with low light transmittance making it an excellent constituent of sunscreen cosmetic creams (Chen et al., 2018; Qian et al., 2017).

Starch is another plant-derived semicrystalline polymer that exists in the nanoscale in the form of starch nanocrystals (SNC) and starch nanoparticles (SNP), and its nanostructures may go up to 1000 nm scale (Tagliapietra et al., 2021), as shown in Fig. 8(q-t). SNC is considered to be highly crystalline smaller starch granules obtained by acid hydrolysis associated with the amyllose content to the greater organization of polymeric starch chains, hence depending on the botanical sources. SNP consists of crystalline as well as amorphous regions and can be obtained by the usage of organic acids, enzymes, and ionic liquids in the processing stages. The size of nanostarch depends on the synthetic methods such as nanoprecipitation, alkaline freezing, crosslinking, and H₂SO₄ hydrolysis, as it is reported that the starch produced by the nanoprecipitation method was 100 nm granules, while hydrolysis with H₂SO₄ gave 800 nm granules (Tagliapietra et al., 2021). Starch nanoparticles are known for their application as stabilizers in Pickering emulsions, where the size and zeta potential of the nanoparticles are important parameters for the stability of emulsions (Shao et al., 2018). Another ongoing research on testing biocompatible starch nanoparticles as...
4.4. Biocomposites

4.4.1. Environmental remediation

With the steep rise in the world’s water consumption and increasing water demand for agriculture, household, and industrial activities, water and wastewater remediation has become central to safeguarding human and environmental health. Lignocellulosic biomass is a sustainable and eco-friendly resource for preparing high-performance biochar and other biocomposites for environmental remediation (Table 1). Biochar is a renewable and industrially viable adsorptive material with high surface area, carbon content, and porous structure made by thermochemical treatment of lignocellulosic residues from agriculture, aquatic, forests, and herbaceous stocks. The production of biochar involves any of the three decomposition processes, namely, pyrolysis (in the presence or absence of oxygen), hydrothermal carbonization, and gasification, and there exist numerous ways of modifying biochar that add to its functionalities and enhancing removal capacity toward a variety of water and air pollutants (Yaashkiaa et al., 2019). Physical activation includes passing steam for creating functional groups (OH, COOH, phenolic, etc.) on the biochar surface or treating the biochar with inorganic acids or alkali hydroxides to induce porosity of biochar as per the biological activation method. Another way to make high-performance modified biochar is by producing coated biocomposite with nanomaterials such as graphene, CNT, graphene oxide, metal oxide nanoparticles, and so on (Shukla et al., 2021). Factors such as the type of feedstock, processing time, heating rate, and pyrolysis temperature can determine the quality and applicability of synthesized biochar. The common ways of modification or activation of biochar can be carried out by physical, chemical, and biological processes. Biochar or modified biochar has been extensively tested for the removal of inorganic (heavy metals, anions) and organic pollutants (dyes, pesticides, antibiotics, emerging organics) from water or wastewater. The material interacts with these contaminants by various mechanisms electrostatic attraction/repulsion, polar, non-polar, and hydrophobic interactions, cation/anion exchange, surface complexity, and precipitation. Luffa, a natural fiber belonging to the Cucurbitaceae family, is a source of lignocellulose that has been used for making biochar and composites such as Luffa/sodium dodecyl sulfate anionic surfactant, nano-Zn modified Luffa sponge, Fe-Luffa activated carbon, etc. have been tested for the removal of Cu (II), Pb (II), Cd (II), MB, malachite green, U (VI), Cr (VI), and more.

Norfluracin, and so on show moderate to high adsorption capacities (Khadir et al., 2021). Another study was conducted on the influence of cellulose and lignin content of tangerine peels (TP) derived biochar on its structural characteristics and catalytic activity towards peroxymonosulfate (PMS) activation essential for phenol degradation in water (Meng et al., 2020). It showed that the lignin-rich biochar has microfibrils-bulk type morphology with lesser adsorption capacity, while cellulose-rich biochar has sheet-like morphology with less oxygen and more ketonic groups on the surface that facilitates higher adsorption characteristics. Biochar is also dissolved in chlorides, nitrates, or oxides of Mg, Al, Ca, Mn, Zn, Fe, Co, etc., followed by pyrolysis for obtaining chemically activated or magnetic biochar (Yaashkiaa et al., 2019). Biomass pretreatment by anaerobic digestion or other bacteria followed by pyrolysis has been shown to increase cation adsorption capacity, hydrophobicity, and porosity of biochar as per the biological activation method. Another

Table 1
Examples of modified and non-modified lignocellulosic material used for environmental remediation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Modification</th>
<th>Target pollutant</th>
<th>Uptake capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochar</td>
<td>Corn stover</td>
<td>Pristine, pyrolyzed at 600</td>
<td>Fluoride</td>
<td>6.42 mg/g</td>
<td>Mohan et al. (2014)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Rice husk</td>
<td>Iron oxide was treated, and pyrolyzed at 550</td>
<td>As (V)</td>
<td>1.15 mg/g</td>
<td>Cope et al. (2014)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Bagasse</td>
<td>Zinc-nitrate treated, pyrolyzed at 450</td>
<td>Cr (VI)</td>
<td>102.66 mg/g</td>
<td>Gan et al. (2015)</td>
</tr>
<tr>
<td>Activated biochar</td>
<td>Food waste</td>
<td>Anaerobic digestion, pyrolyzed at 400</td>
<td>Methylene blue</td>
<td>9.50 mg/g</td>
<td>Sun et al. (2013)</td>
</tr>
<tr>
<td>Natural absorbent</td>
<td>Luffa Cylindrica</td>
<td>–</td>
<td>Cd (II)</td>
<td>6.77 mg/g</td>
<td>Shahidi et al. (2015)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Pinewood chip</td>
<td>CeCl2 impregnation</td>
<td>Levofoxacin</td>
<td>7.72 mg/g</td>
<td>Yi et al. (2018)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Wheat straw</td>
<td>ZnCl2 and H3PO4</td>
<td>Atrazine</td>
<td>150-200 mg/g</td>
<td>Zhao et al. (2018)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Rice straw</td>
<td>Fe (NO3)3</td>
<td>Anisole, phenol, guaiacol</td>
<td>70.4, 17.2, 23.3 mg/g</td>
<td>Li et al. (2017)</td>
</tr>
<tr>
<td>Modified biochar</td>
<td>Corn cob</td>
<td>FeCl3</td>
<td>Nitrate</td>
<td>32.33 mg/g</td>
<td>Long et al. (2019)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Coconut shell</td>
<td>Steam, 850 °C</td>
<td>DCM</td>
<td>2.69 mmol/g</td>
<td>Comer et al. (2006)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Coconut shell</td>
<td>Steam, 800 °C Cu, 3 wt%</td>
<td>SO2</td>
<td>24 mg/g</td>
<td>Tieng and Wey (2004)</td>
</tr>
<tr>
<td>(MB-IA)/g-MNCC</td>
<td>Nanocellulose</td>
<td>graft co-polymerization of itaconic acid onto magnetite nanocellulose (MNCC) using EGDMA as a cross-linking agent and K2S2O8 as free radical initiator</td>
<td>Co (II)</td>
<td>349.62 mg/g</td>
<td>Anirudhan et al. (2019)</td>
</tr>
<tr>
<td>Modified cellulose</td>
<td>Bacterial cellulose</td>
<td>Epichlorohydrin + diethylentriamine</td>
<td>Cu (II), Pb (II)</td>
<td>84.63 mg/g</td>
<td>Shen et al. (2009)</td>
</tr>
<tr>
<td>CNC-COOH</td>
<td>Cellulose nanocrystals</td>
<td>Esterification with maleic anhydride</td>
<td>Crystal violet</td>
<td>244 mg/g</td>
<td>Qiao et al. (2015)</td>
</tr>
<tr>
<td>TEMPO CNF-PEI</td>
<td>Nano fibrillated cellulose</td>
<td>Oxidized cellulose nanofibrils modified with PEI</td>
<td>Cu (II)</td>
<td>52.3 mg/g</td>
<td>Zhang et al. (2016)</td>
</tr>
</tbody>
</table>
Red (CR)) and Cr (VI) from water under visible light (Djellabi et al., 2019). Another example of a nanocatalyst Cu + Co@OPF is a mixed metal nanoparticle decorated on LCB (oil palm frond, OPF) produced by the wetness co-impregnation method for wastewater treatment (Sohni et al., 2018). It has been used for catalytic reduction of organic pollutants such as Congo red (CR), Methyl orange (MO), Rhodamine B (RB), Methylene blue (MB), and different nitrophenols such as ortho-nitrophenol (ONP), meta-nitrophenol (MNP), para-nitrophenol (PNP), 2, 4-dinitrophenol (DNP), where the order of pollutant removal was observed as MO > RB > MB > CR in case of dyes and PNP > MNP > ONP > DNP for nitrophenols, respectively. The rapid breakdown of toxic organic pollutants was achieved using NaBH₄ as a hydrogen and electron source. Composite made of saw dust-based biochar with kaolinite and bronsted clay could efficiently treat water by removing total dissolved solids (TDS), total hardness (TH), and turbidity with a moderate to high removal rate (Chaokura et al., 2020).

Micro/nanocellulose derived from lignocellulosic biomass has emerged as an attractive choice in the diverse application of water remediation due to the flexibility of surface functionalization and modification, stability, and biocompatibility. It has been widely explored as a material used alone or as a constituent of composites used in the form of bio sorbents, aerogel and hydrogel adsorbents, ion exchange materials, flocculants, photocatalysts, filtration, and RO membranes for water and wastewater treatment (Sharma et al., 2021). Apart from its hydrophilic nature and controllable surface chemistry, nanocellulose shows potential for reduction of bio/organic fouling, thus being a suitable option for solving the basic challenges of membrane technology (Voisin et al., 2017). These membranes have shown efficiency in the removal of heavy metals, anions, organics, pathogens, etc., and often proved to function better at relatively high flux and low pressure than conventional commercial membranes.

Activated carbon derived from lignocellulosic biomass is a versatile option for its application in trapping air pollutants such as volatile organic compounds (VOCs), particulate matter, and harmful gases (SO₂, NOₓ, H₂S, etc.) (Loomis et al., 2013). The sources of these pollutants can be industries, power plants, combustion of biomass and fossil fuel, transportation, etc. To overcome this problem, carbon activated employing steam/CO₂chemicals impregnation at 500–1000 °C is employed (Nor et al., 2013). Activation carbon used for gas phase applications usually has a very high surface area and pore volume. For example, activated carbon derived from coconut shell prepared by steam activation exhibited a high surface area of 2278 m²/g and pore volume of 1.13 cm³/g was tested for adsorption of VOCs (dichloromethane and trichloroethylene) that showed uptake capacity of 2.69 mmol/g and 6.89 mmol/g for DCM and TCE, respectively (Connier et al., 2006). Biomass impregnated with transition metals such as iron, cobalt, nickel, and copper was tested for the removal of toluene and NO simultaneously, where copper-impregnated activated carbon showed the highest adsorption capacity (Lu and Wey, 2007).

### 4.4.2. Sustainable inks for additive manufacturing

The most significant polysaccharide in plant structure is cellulose, which is one of the most plentiful biopolymers on earth. Cellulose based biocomposites are used as material extrusion in 3D printing matrices due to cellulose fiber’s excellent mechanical properties (Wang, Q. et al., 2018a, b). The principal privilege of cellulose-based materials for 3D printing is interconnected to their availability, processability, aspect ratio, and compatibility with viscoelastic rheological properties. Correspondingly, cellulose nanocrystals and nanofibers have been used as reinforcements in inks designed for additive manufacturing (Kuhn and Camarero-Espinosa, 2021). Nanocellulose’s high orientation degree encourages tailored reflexes to mechanical forces, similar to the design principles encountered in wood. Furthermore, nanocellulose is capable of demonstrating thixotropic and shear-thinning properties needed for extrudable inks. Siqueira et al. (2017) have developed viscoelastic nanocellulose-based inks for 3D printing by simply distributing the extracted CNC particles in water. Likewise, Kam et al. (2019) have printed complex shapes formed of wood composites by utilizing a by-product of wood industries called wood flour extracted from smashed pine, maple, or eucalyptus mixed with a binder made of cellulose which delivers the ink shear-thinning effects. These two inks can be gained from factory by-products, and the mechanical properties of the printed composites are similar to natural woods. Besides, Li et al. (2020) have printed different objects constructed of cellulose nanofibers with suitable properties by using some amount of the UV cross-linkable polymer.

Fig. 9a–c shows the 3D printed cellulose nanocrystal aerogels with well-controlled and dual porous structures. The inks at various weight percents of cellulose nanocrystals were designed and 3D printed into complicated 3D structures. According to Fig. 9e, the average structural pore size is 600 μm, and the spontaneous pore size distribution ranges from 20 to 800 μm (Li et al., 2017). Fig. 9d demonstrates various types of 3D printing systems suitable for lignocellulose-based materials. To deposit filament, piston, pneumatic, or screw dispensers mounted on a motion-controlled positioner or dispense robot is used. However, specific viscoelastic and rheological qualities are necessary for the printing materials, such as lignocellulosic-based inks, to be smoothly extruded from the printing head. The vast majority of ink solutions created with these materials exhibit a shear-thinning rheological behavior marked by declining viscosity with a rising shear rate. Fig. 9e demonstrates SEM images of cellulose nanofibers (CNF) and cross-linked CNFs with different metallic cations as printing inks, as well as successfully printed cubes (Miętner et al., 2021).

For uses such as tissue engineering and biomedical applications, the suspensions of cellulose with shear-thinning characteristics have been printed utilizing a direct writing approach. This method is useful for direct paste writing, which is suitable for Cellulose-based suspensions. In 3D printing, cellulose-based suspensions’ rheological characteristics are crucial. To prevent viscous flow ink and the deterioration of the printed material, the stability of viscous behavior, which is temperature-dependent, is required. A lot of studies have been done on understanding coagulation problems and colloidal stability while printing hydraulic suspensions in three dimensions (Hubbe et al., 2017). Cellulose-based materials are also being selected as 3D printing ink for photopolymerization techniques, as a supplementary step in direct writing, with applications in biomedical materials. The preliminary goal of using cellulose in photopolymerization methods is to enhance the thermal stability and mechanical properties of the 3D-printed final product (Mohan et al., 2020). There are a few other methods, such as digital light processing (DLP) and stereolithography (SLA) which are used to print cellulose-based biocomposites containing photoreactive resins. DLP and SLA can design and produce bone replacements, bone cement, and medicine delivery devices using cellulose and photoreactive bioreins as the main constituents (Li et al., 2019; Mohan et al., 2020).

The combination of cellulose with other bio-based polymers like alginites and gelatines has been broadly studied for the formulation of hydrogels and aerogels (Fazzelli et al., 2022a; Françon et al., 2020; Håkansson et al., 2016; Li et al., 2018; Zhang et al., 2020) for 3D printing, expanding the use of cellulose in medical/tissue engineering, load bearing, and electronics, and wearable applications (Sultan et al., 2017; Sydney Gladman et al., 2016). Current advancements have also been made in 3D printing of cellulose biocomposites with excellent properties using either pure dissolved cellulose (Jiang et al., 2021) or cellulose by-products like hydroxyethyl cellulose (HEC), methylcellulose (MC), ethyl cellulose (EC), carboxymethyl cellulose (CMC), and hydroxypropyl methylcellulose (HPMC) (Das et al., 2019). In circumstances where stimuli-responsive qualities are advantageous, a comparable potential has been shown in the field of 4D printing employing cellulose (Mulakkal et al., 2018; Sydney Gladman et al., 2016). Because of the wide variety of cellulose-based materials accessible in varied sizes, forms, and qualities, cellulose may be used for a variety of purposes in 3D printing, including binder, rheology modifier, matrix, excipient, and reinforcement (Xu et al., 2018). Table 2 provides a
Fig. 9. 3D printed dual pore scaffold aerogel with 20 wt% CNC for (a) a cube and (b) a human nose model, and (c) its corresponding SEM images (Li et al., 2017). (d) Different techniques for 3D printing of lignocellulosic-based materials. (e) Representative SEM images of CNF and cross-link CNFs with various metallic cations as inks and their printed samples (Mietner et al., 2021).
and purification. Most of the studies have emphasized cellulose, lignin, and hemicellulose. These component-based products on wound dressings..

Table 2 Cellulose-based materials in 3D printing (Kalia et al., 2011; Xu et al., 2018).

<table>
<thead>
<tr>
<th>Target</th>
<th>Properties needed to approach the target</th>
<th>Applications in additive manufacturing</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>Cellulose contains shear-thinning properties that are a suitable option for a binder for 3D printing powders.</td>
<td>A paste’s rheology resembles that of the binder in 3D printing ink. A successful print is made possible by the cellulose’s shear-thinning effect when used as a binder.</td>
<td>(Lenke and Treml, 2013; Tanwilaisiri et al., 2016)</td>
</tr>
<tr>
<td>Rheology modifier</td>
<td>Cellulose maintains the proper rheological properties for 3D printing, allowing the ink to flow smoothly at high shear rates and solidify quickly when printing is complete.</td>
<td>(Siqueira et al., 2017; Sydney Gladman et al., 2016)</td>
<td></td>
</tr>
<tr>
<td>Matrix</td>
<td>Dissolved cellulose shows high viscosity and demonstrates shear-thinning.</td>
<td>For accurate, consistent prints using 3D printing processes like material extrusion, high-viscosity cellulose is the best material.</td>
<td>(Kalia et al., 2011; Wang, H. et al., 2018a,b)</td>
</tr>
<tr>
<td>Excipient</td>
<td>Cellulose has a hydrophilic nature, and it allows for achieving steady swelling in water.</td>
<td>This feature can be utilized in applications like 4D printing and drug delivery.</td>
<td>(Gooole and Amigbi, 2016; Kanstra et al., 2006; Khalid et al., 2014; Khalid and Arifi, 2022; Kumar et al., 2022)</td>
</tr>
<tr>
<td>Reinforcement</td>
<td>Cellulose fibers demonstrate high stiffness, high strength, and low density.</td>
<td>Cellulose fibers as reinforcement in the thermoplastic matrices are generally used as formulations or filaments. 3D-printed cellulose composites have demonstrated enhanced mechanical properties.</td>
<td>(Hu et al., 2015; Müller et al., 2020; Sultan and Mathew, 2018)</td>
</tr>
</tbody>
</table>

summarized outline of the cellulose used in the 3D printing technique and related applications and properties. The scientific community’s interest in creating and defining novel techniques and materials has been considerably increased by this potential for using cellulose in 3D printing.

4.4.3. Biomedical applications

Lignocellulosic materials are enriched sources of natural components which are necessary for standard medicine and have been recreating a significant role in drug delivery systems and medicine. These subjects, with all their pharmacological and chemical challenges, are always acquiring much more concentration in the scientific community. The current special subject encapsulates a few of the most responsible studies in the field of lignocellulosic materials’ use in medicine. The mentioned research covers the development of separation, extraction, and purification. Most of the studies have emphasized cellulose, lignin, and hemicellulose to be used for medicinal purposes and drug applications. Some outstanding research has focused on developing and constructing novel drug delivery systems based on lignocellulosic materials (Wijaya et al., 2021). Dai and Si (2019), discussed the significant discoveries on the drug delivery techniques of cellulose-based materials. Although cellulose still offers certain benefits, the structure of raw cellulose has several inherent flaws. Therefore, different kinds of cellulose-based nano-drug delivery systems used for pharmacodynamic actions and functionalization have been investigated, containing prodrugs, solid nanoparticles (NPs), and amphiphilic NPs. These impressive studies nominated many methods for overwhelming the free drug molecule deficiencies such as suboptimal pharmaco-kinetics, inferior solubility, and surplus toxicity. Among all the techniques explained in this review, amphiphilic NPs (containing cellulose/lipophilic drug NPs) are the most repeatedly employed for producing cellulose-based Nano-Drug delivery systems. Although there are several challenges with the research on cellulose-based nano-drug delivery systems, including the lack of a thorough physicochemical report, a thorough understanding of how the materials described interact with cells both in-vitro and in-vivo, and parameter optimization. Besides, in the study by Lin et al. (2018), the function of hemicellulose in pharmaceutical and medical applications is illustrated. The focus of this collaboration is on the creation of plant-derived degraded hemicellulose, extracted hemicellulose, and hemicellulose derivatives. The immunological principles and antimicrobial properties of plain hemicellulose comprising xylan, xyloglucan, mannann, and β-glucan are shown. Hemicellulose degradation products such as xylitol, xylooligosaccharides, xylose, mannose, and arabinoise offer some excellent advantages for increasing bodily processes. The changes in hemicellulose, such as etherification and esterification can enlarge the medical application in scaffolds. In addition, the study delivers the benefits of hemicellulose composites and hemicellulose-based products on wound dressings.

Zhang, L. et al. (2019a,b) study lignocellulosic biomass, and its chemical components are spotlighted as possible choices for applications in biomedical. As a matter of fact, the pre-treatment techniques for extracting cellulose, lignin, and hemicellulose from lignocellulosic biomass through steam explosion, milling, microwave, irradiation, ammonia fiber explosion, alkaline hydrolysis, supercritical CO₂ oxidation, liquid hot water pre-treatment, acid hydrolyses, and biological treatments, and their biological applications like biosensor, tissue engineering, drug delivery and so on are lined out. Also, explore the potential of evaluating lignocellulose to produce high-value pharmaceuticals utilizing current biotechnology and notable tools in metabolic engineering, genomics, and synthetic biology. Biofuel research has recently focused on exploiting cellulosic waste, which makes up a sizable portion of both industrial and agricultural biomass. Based on their findings, they address current advances in genomic research of biological lignocellulose species (particularly fungus and bacteria), as well as how these studies promote the development of the next generation of carbohydrate-active enzymes and lignin-degrading enzymes. Following that, the authors investigate the trendiest themes in metabolic engineering to produce biological products. Connecting the vanguard genomic research with accomplishments in synthetic biology and metabolic engineering by managing either a single microbe or a microbial consortium for the rapid introduction of pharmaceuticals from lignocellulose, the authors demonstrate the future trends of bioprocess development and examine how lignocellulosic materials are often used in drug delivery systems (DDS). As a natural polymer, cellulose has outstanding optical, rheological, and mechanical characteristics and is simple to be modified. Oxidation of cellulose surface groups, etherification, and esterification at their hydroxyl groups are the typical changes in lignocellulosic materials. Different sizes of cellulose-based production, made via chemical, mechanical, and enzymatic treatments, and their compounds maintain special properties. Drug solubility behaviour can be altered by cellulose and its by-products, resulting in a variety of strategies for controlling drug release behaviour. The many classic and cutting-edge uses of cellulose and its derivatives in medication delivery systems are thoroughly examined, wishing to investigate
their possible application in the creation of novel dosage conditions for pharmaceuticals. In the published paper by Khan et al. (2019), with special emphasis on drug loading and release from chitosan-based materials, the suitability and novel drug delivery applications of chitosan are highlighted. This study demonstrates how in-depth analyses of the polymer’s promising non-toxicity, biodegradability, biocompatibility, and molecular weight variation have made it a desirable candidate for developing new DDS with a variety of progressive therapeutic applications, such as gene delivery, organ-specific drug delivery, DNA-based drugs, and cancer drug carrier.

4.4.4. Cleaner production and waste recycling

The final application of lignocellulosic-based materials nowadays encounters the restriction specifically on the market for valorizing lignocellulosic surplus, particularly on the pre-treatment like the cost-effective and quick production of cellulose (Sindhu et al., 2016). Undoubtedly, except for the typical mesophilic anaerobic digestion, most contemporary lignocellulose materials-related methods in practical biorefineries have reached the end of their pilot-scale study (Fazeli et al., 2022b). It may be necessary to effectively dissolve the lignocellulosic complex structure to access its main constituents, including cellulose, hemicellulose, and lignin (Pazhany and Henry, 2019). Based on the gathered information by Sánchez-Gutiérrez et al. (2021), Most lignocellulosic-based residues include 30–50% cellulose, whereas lignin and hemicellulose contain 10–20% and 20–30%, respectively, however, the amounts may vary depending on the types and portions of the plants (Sharma et al., 2019). Hemicellulose and cellulose are monosaccharide-based natural polymers, whereas lignin is an aromatic polymer that is naturally generated from phenylpropanoids (Sánchez, 2009).

The available methods to recycle the lignocellulosic residue consist of hydrolysis, pretreatment, fermentation, and post-treatment, like liquid-liquid separation or distillation. Pretreatment, which comes first, aims to lessen the recalcitrance of lignocellulosic materials by destroying their structure, reducing the crystallinity of the cellulose, and separating their constituent parts (like the removal of lignin content). Pretreatment of lignocellulosic materials in biorefineries typically costs around half of the budget (Sindhu et al., 2016). Numerous pretreatment methods are known nowadays, but each technique contains important weaknesses in practice. It is good to mention that physical techniques such as ammonia fiber explosion and steam explosion are energy-consuming, and chemical processes such as acid, alkaline, and hot water generate wastewater that needs additional attention.

According to the complex structure of cellulose, hemicellulose, and lignin, the degradations of these components are always a challenge, and it is considered the second step of recycling. Even though an enzymatic method may hydrolyze cellulose and hemicellulose, effective technology for the modification of lignin is limited since it uses combustion to provide energy (Vangeel et al., 2020). Due to the benchmark designed for the modification of lignin, the pretreatment is to increase the surface area, decrease the crystallinity, and remove the hemicellulose from the cellulose to make it easier to hydrolyze (da Costa Sousa et al., 2009). Hemicellulose, a branched polymer typically composed of xylose monomers along with C5 and C6 sugars, covers the surface of the cellulose fibrils. Pretreatment of LCB with a dilute acid removes the hemicellulose and partially removes lignin from LCB. The deconstruction of hemicelluloses via dilute acid pretreatment yields a cocktail of monosaccharides, that largely consists of xylose. The biological processing of xylose yields two significant compounds, xylitol, and ethanol (Agbor et al., 2011). However, the conversion of xylose obtained from the hydrolysis of hemicellulose is more difficult compared to glucose released by hydrolysis. Furfural is among the important chemical compound wide range of applications that can be extracted from xylose. Around 60% of the produced furfural is utilized to produce furfuryl alcohol (tetrhydrofuran and tetrahydrofurfuryl alcohol). The remaining 40% of furfural is largely used in industries like oil refining, agrochemical, pharmaceutical, and plastics (Rosatella et al., 2011). However, the industrial production of furfural is still confronted by several constraints that are limiting the industrial potential of furfural. Among these, a) the occurrence of side reactions involving furfural and sugars; b) cross polymerization among xylose, furfural, and other intermediate molecules yielding soluble polymers and insoluble humins, c) fragmentations of furfural in an acidic environment yielding formic acid, formaldehyde, and lactic acid, etc. The use of a solid acid catalyst system or developing a biphasic reaction system to produce furfural are among the proposed approaches that can help on the industrial scale production of furfural.

Hydroxymethyl furfural (HMF) is a flexible platform chemical obtained from biomass that can be utilized to manufacture a wide range of compounds that are currently produced using petroleum (Steinbach et al., 2017). HMF is synthesized from C6 sugars via acid (heterogenous or homogenous acids) catalyzed dehydration. HMF is an excellent material for chemical modifications, thanks to hydroxyl and aldehyde functional groups. Low reactivity arising from the formation of humin is a major challenge during the synthesis of HMF. A detailed synthesis pathway and the effect of different acid catalyst systems have been discussed comprehensively in several review articles (Rosatella et al., 2011).

5. Final remarks

The use of materials previously considered by-products, such as lignocellulose from agricultural side streams, is extremely important for the world economy and the preservation of the environment, seeking to maximize the use of natural resources, thus boosting the practice of circular economy. Currently, an accelerated investment is undergoing to develop lignocellulose-related products and technologies. However, more serious investments are needed for the maturation and commercialization of the currently available processing and product development approaches. The valorization processes and technologies involved
in this process need to be cost-effective so that the products coming out from lignocellulose biomass valorization can compete in the current market. An integrated biorefinery approach is vital to make the entire value chain of lignocellulosic biomass. Avenues of cost optimization include cost-effective pretreatment approaches, the development of efficient enzymes, the complete translation of polysaccharides into sugars, and process integration. Lignocellulosic biomass is a complex and recalcitrant resource, which imposes challenges for the efficient fractionation and utilization of their macromolecular components. Efficient pre-treatments should be developed for each specific biomass type, aiming to maximize the recovery and mass balances of the cellulose, hemicellulose, and lignin components. Moreover, the development of chemo-enzymatic approaches to transform the lignocellulose components into new materials with targeted properties constitutes an important challenge. In recent years, new mild and selective processes to functionalize the surface of cellulosic fibers and isolated hemicelluloses have emerged, aiming to upgrade their properties toward the desired final applications. Bioplastics, from renewable sources or not, usually have higher production costs and, not rarely, lower final properties than traditional polymers. Therefore, biomass from agricultural waste has attracted the attention of researchers worldwide, aiming to produce cheaper bioplastics. The aromatic nature of lignin has been extensively explored to obtain better mechanical properties. The nanomaterials obtained from lignocellulosic are not only interesting from a research viewpoint, but they also possess a very wide scope of applications with improved functionality and performance. Their utilization in producing biocomposites which have in turn found applicability in environmental remediation, additive manufacturing, biomedical materials, and so on have been discussed in this review. Apart from producing advanced functional materials, nanotechnology also has a huge potential in devising pretreatment methods for lignocellulosic biomass as novel and economically viable alternatives to conventional methods.

Credit authorship contribution statement

Muhammad Mujtaba: Conceptualization, Investigation, Writing - Original draft, Reviewing and Editing; Leonardo Fraceto: Conceptualization, Investigation, Writing - Original draft, Reviewing and Editing; Mahyar Fazeli: Investigation, Writing - Original draft; Sritama Mukherjee: Investigation, Writing - Original draft; Susilaine Maira Savassa: Investigation, Writing - Original draft; Gerson Araujo de Menezes: Investigation, Writing - Original draft; Anderson do Espírito Santo Pereira: Investigation, Writing - Original draft; Sandro Domini Mancini: Investigation, Writing - Original draft; Juhu Lipponen: Investigation, Writing - Original draft; Francisco Vilaplana: Writing - Original draft, Investigation, Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

All authors are grateful to FinELib and VTT Technical Research Centre of Finland for the support to make this article open access. L. F., S. M. S., G. A. M., A. E. S. P., and S. D. M., are grateful to the São Paulo Research Foundation (FAPESP - #2017/21004-5), Coordination for the Improvement of Higher Education Personnel (Capes), and the National Council for Scientific and Technological Development (CNPq).

References


Stephenson, P., DAMerell, A., 2022. Bioreour. and circular economy approaches need to enhance the focus on biodiversity to achieve sustainability. Sustainability (14), 10645.


